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Published in:
Journal of Physics: Conference Series (Online)

Link to article, DOI:
10.1088/1742-6596/522/1/012010

Publication date:
2014

Document Version
Publisher's PDF, also known as Version of record

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2014 J. Phys.: Conf. Ser. 522 012010

(http://iopscience.iop.org/1742-6596/522/1/012010)

Low-pressure ETEM Studies of Au assisted MgO Nanorod Growth

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Abstract. Environmental transmission electron microscopy (ETEM) studies MgO nanorod growth from Au catalyst nanoparticles in a controlled gas atmosphere have been performed, in order to elucidate the mobility of Au surface atoms and the configuration of the Au/MgO interface. MgO nanorod growth is driven by the electron beam and found to be strongly dependent on the gaseous environment in the microscope and electron beam current density.

1. Introduction

Nanometer sized Au particles supported on MgO (100) surfaces have been used as model catalyst for CO oxidation at room temperature [1,2]. The exact morphology and size of the particles are strongly linked to the activity of the reaction as shown theoretically by McKenna *et al.* [3]. Environmental TEM is an excellent tool to study individual nanoparticles under conditions similar to their working environment [4]. However, the highly energetic electron beam might influence the sample in undesirable ways. The focussed electron beam has earlier been shown to cause growth of MgO nanorods on the MgO support under high dose irradiation in high vacuum [5,6]. In the present work, the presence of residual gas in the microscope column is shown to enhance the MgO nanorod growth significantly. The growth of MgO nanorods are found at relatively low beam currents compared to earlier work[6]. In order to exploit the opportunities of ETEM on such beam sensitive systems a more systematic approach has to be considered.

2. Experimental Details

MgO smoke particles are produced by combustion of a Mg metal ribbon to form close-to-perfect cubes exposing MgO (100) surfaces. The MgO cubes are collected on a TEM grid by placing the grid in the smoke for a few seconds. Au nanoparticles are deposited on the cubes by sputter-coating for 1s using a Cressington 208 HR Sputter Coater forming 2-6nm epitaxially oriented Au nanoparticles, see inset Fig. 1a.

The samples are investigated in an FEI Titan 80-300kV ETEM equipped with a differential pumping system that allows samples to be exposed to a gaseous environment. Further specifications of the microscope can be found in [3]. Using the differential pumping system rather than the original microscope pumping system consisting of ion getter pumps and a liquid nitrogen cold trap results in a slight degradation of the vacuum. The residual gas in the column is found to be predominantly water by means of mass spectrometry. The samples are studied in this residual gas in the pressure range 10^{-5}Pa to 10^{-4}Pa. All experiments were carried out at room temperature.

3. Results

Figure 1 shows a TEM image of the prepared sample together with a size distribution of the formed Au particles. The sputter coating parameters chosen resulted in nanoparticles with a size below 4nm, giving a realistic model catalyst system.

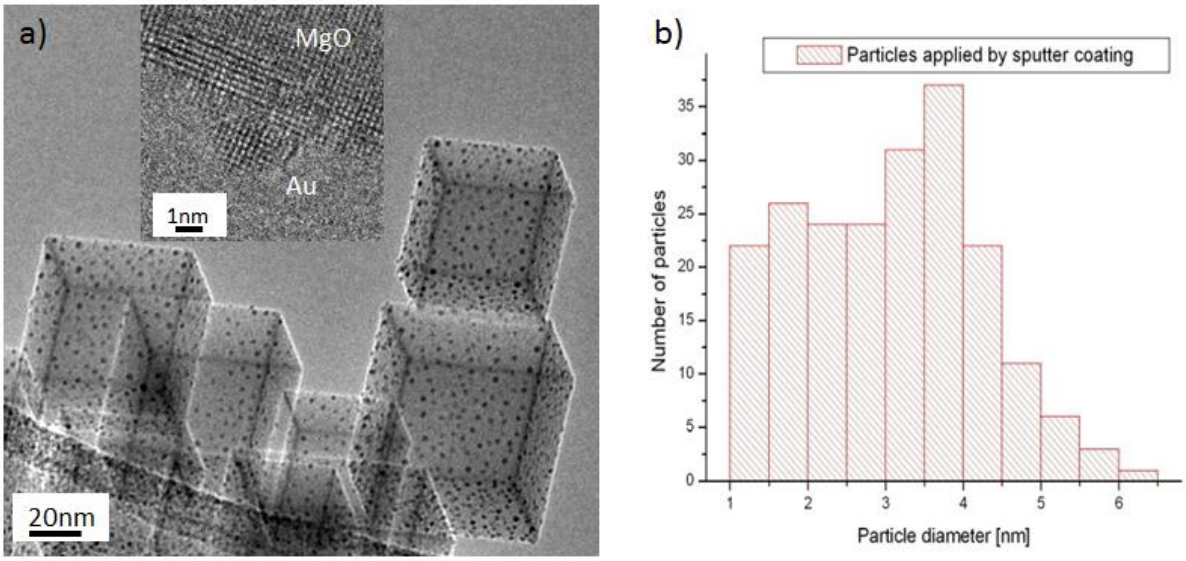

Figure 1. a) TEM micrograph of MgO supported Au nanoparticles. Inset: HRTEM micrograph of MgO supported Au nanoparticle b) Particle size distribution of the Au particles.

MgO and Au are both cubic crystals with a slight mismatch (~3%) in the lattice distance (a_{Au}=4.08Å, a_{MgO}=4.21Å). The Au nanoparticles are epitaxially oriented as seen in the inset in Fig. 1a. When the samples are illuminated by the electron beam, nanorods grow at the Au/MgO interface. Eventually the Au particles disappear and the nanorods dissolve in the electron beam. Figure 2a shows stills from a video capturing the growth and dissolution process of the nanorods. The measured nanorod length during growth and dissolution is presented in Fig. 2b.

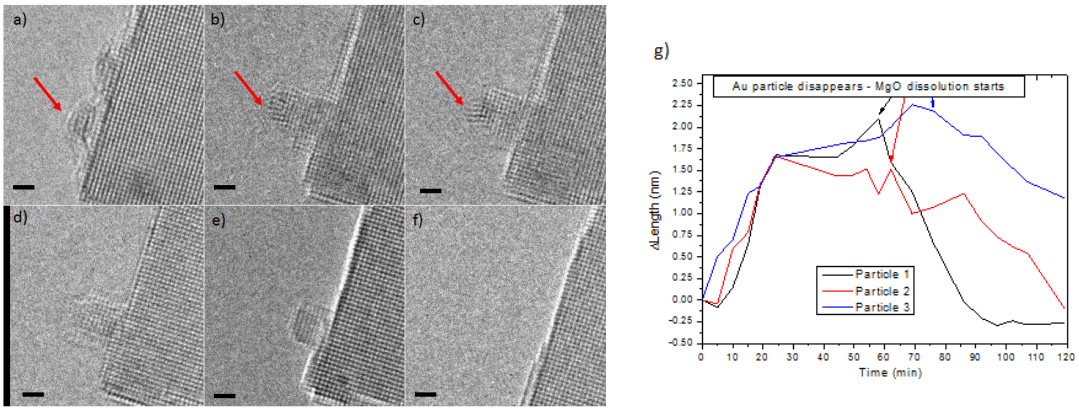

Figure 2. a)-f) HRTEM micrographs as stills from an image sequence showing Au-assisted growth of a MgO nanorod. When the Au particle disappears, the nanorod dissolves. The red arrows indicate the Au nanoparticle. P=10^{-4}Pa, j=1A/cm². The scalebars are 1 nm. g) Tracking the MgO nanorods grown at P=10^{-4}Pa and j=1A/cm².

A detailed view of the Au/MgO interface during growth can be found in Fig. 3. The time interval between each image is 3s with the particle/nanorod interface highlighted to illustrate the dynamics of the kinked interface.
Figure 4 summarizes our findings on the effect of the electron dose and water vapour pressure on the sample. The images are acquired after approximately 30min of electron irradiation in each case. In general higher electron beam current density (Figs 4c and d) increases the structural changes of the MgO surface. Increasing the (water) pressure in the microscope affects the mobility of the MgO species and results in increased roughness of the MgO (100) surfaces. The dashed lines in Fig. 4 indicate the layer that underwent structural change during electron irradiation.

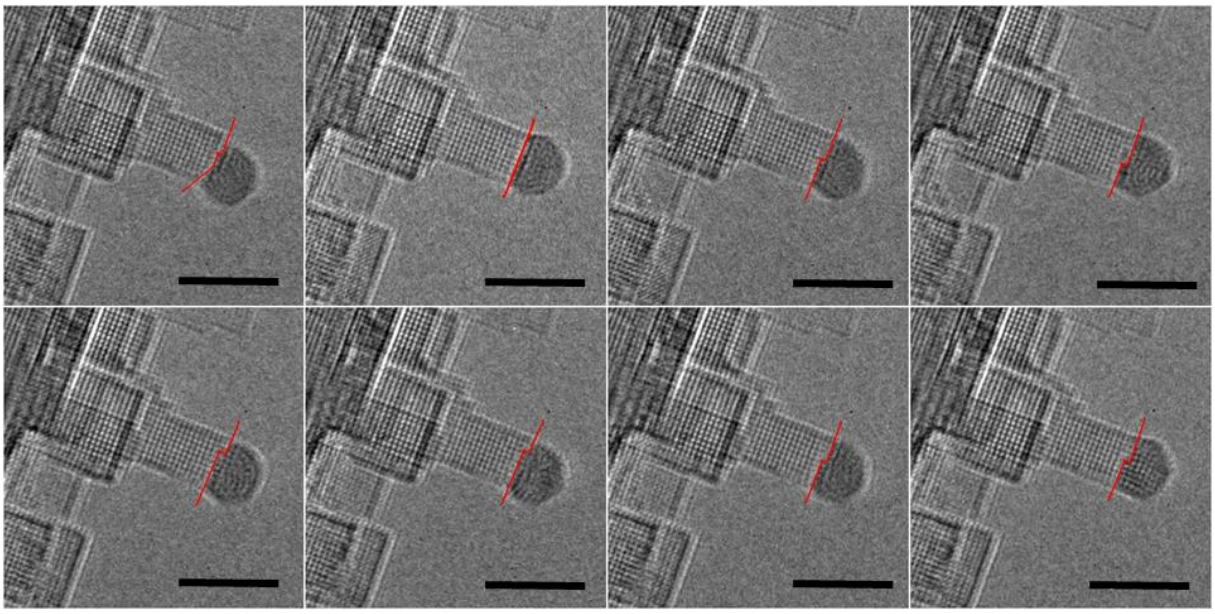

Figure 3. HRTEM micrograph of one nanorod and the attached Au particle in a series of stills separated by 3s. P=10^{-4}Pa, j=1A/cm². Scalebars are 5nm.

4. Discussion

The growth and dissolution observed in Fig. 2 have been quantified in order to illustrate the dynamical mechanism. After initial growth the nanorods reach a point of steady state where the mobility of the Au particle increases.
The shrinkage of the Au nanoparticles observed prior to the final dissolution of the MgO nanorods indicates Ostwald ripening of the Au nanoparticles. The diffusion barrier of Au atoms at the surface is relatively small as is the case for most metals and metal oxides [3]. Without Au as a collection agent for the MgO species the nanorods dissolve due to the increased mobility of MgO at the tip.
The longer nanorods typically have a diameter comparable to the growth particle at the tip. Even though the Au particles are highly mobile and in principle can act as collection point over a larger area resulting in wider features at the MgO surface, the competing dissolution of the MgO favours nanorods with diameters similar to the Au nanoparticles. It is evident that the Au nanoparticle is highly mobile, moving perpendicular to the growth direction of the nanorod in discrete atomic steps dictated by the epitaxial relationship between Au and MgO. Figure 3 clearly shows the mobility of the Au particle and the Au/MgO interface illustrating the Au/MgO interface to act as a collection point (due to negatively charged metal particles) where the highly mobile MgO species are trapped and recrystallize in rods.
The structural changes on the MgO surface depends on the electron beam current density and the pressure. The apparent roughness of the MgO surfaces after 30min. electron irradiation ranges from monolayer roughness to 3-4nm as indicated in Fig. 4. At low pressure (P=10^{-5}Pa) and relative low electron dose rate (10^{-15}A/nm^2) the surface mobility of MgO species is observed to be relatively small.

Increasing the electron dose or the pressure by leaking in water vapour, increases the mobility on the surface resulting in the formation of kinks and steps. The presence of water species in the surrounding environment influences the charge transfer in the system changing the overall energy landscape and thereby increasing the probability of MgO species getting trapped at the Au/MgO interface.

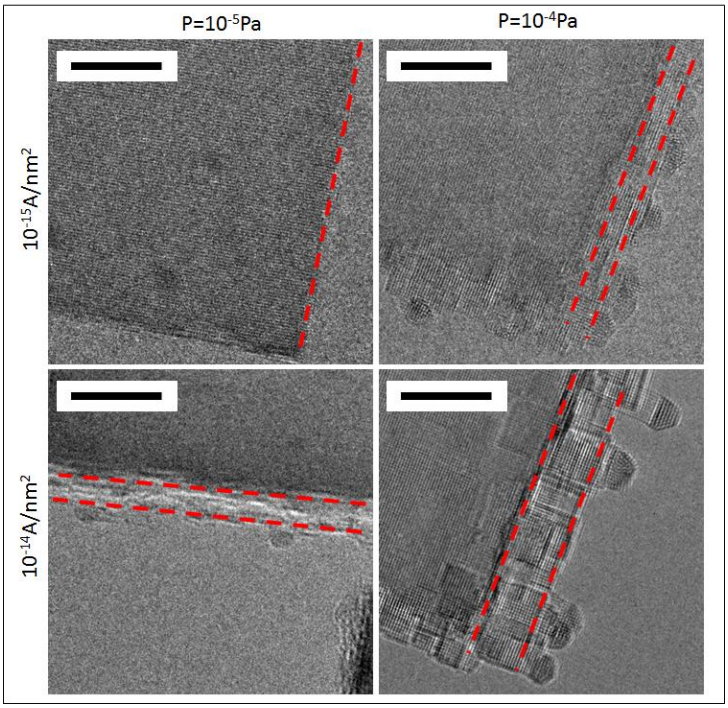

Figure 4. Au/MgO exposed to different electron dose rates at different pressures for approximately 30min in each case. Scale bars are 5nm.

5. Conclusion

The present results of Au nanoparticles on MgO under non-UHV conditions in an electron beam suggest that the mobility of MgO species and Au ability to trap such is strongly dependent on the gaseous surroundings and the electron beam current density. Quasi one-dimensional structures of MgO are grown and stabilized by the Au nanoparticles. As soon as the Au disappears, most likely due to Ostwald ripening, the MgO nanorod dissolves leading to an overall lower surface energy of the MgO cube.
The findings strongly suggest that the electron beam has a severe effect on the observations and materials behaviour especially when gases are involved. A slight increase in pressure in the ETEM compared to conventional TEM strongly enhances the electron beam induced mobility of MgO species at the MgO (100) surfaces.

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